

# TIME-RESOLVED STUDIES OF THE DEVITRIFICATION PROCESS IN METALLIC GLASSES

Devitrification at a rate of 40 K/min was measured in metallic glasses  $\text{Ti}_{34-x}\text{Cu}_{47}\text{Zr}_{11}\text{Ni}_8\text{Si}_x$ . Time-resolved x-ray diffraction detects the formation of nonequilibrium phases that may not be observable with traditional heat-and-quench techniques. Here we demonstrated that the thermal events observed in differential scanning calorimetry do not necessarily correspond to equilibrium phases.

Time-resolved devitrification studies of the metallic glasses  $\text{Ti}_{34-x}\text{Cu}_{47}\text{Zr}_{11}\text{Ni}_8\text{Si}_x$  were performed using a recently developed high-temperature furnace in a Debye-Scherrer geometry. Synchrotron radiation at the Advanced Photon Source (APS) at Argonne National Laboratory was used to follow the devitrification of samples during heating at 40 K/min between 623 and 1073 K. The crystallization behavior observed with structural diffraction data compares well with results from thermal analysis using differential scanning calorimetry (DSC). Samples included bulk metallic glass powders produced by high-pressure gas atomization. At 1073 K, these amorphous alloys evolve to a four-phase microstructure that includes phases that appear to be closely related to  $\text{Cu}_{51}\text{Zr}_{14}$ ,  $\text{CuTi}$ , and  $\text{Cu}_2\text{TiZr}$ . These *in situ* studies revealed the formation of metastable phases that were not observed by conventional heat-and-quench techniques, underscoring the power of time-resolved x-ray diffraction experiments.

The time-resolved studies of the powders were performed with the 6-ID-B beamline at the APS in collaboration with the Midwest Universities Collaborative Access Team (Mu-CAT). The data presented in this study were obtained with an incident energy of 38.33 keV. The atomized powders were loaded into 2-mm-internal-diameter thin-walled amorphous silica tubes. Prior to sealing, the tubes were evacuated to a pressure less than  $10^{-2}$  mbar and then backfilled with Ar. A Debye-Scherrer geometry (with an area detector) for collection of diffracted

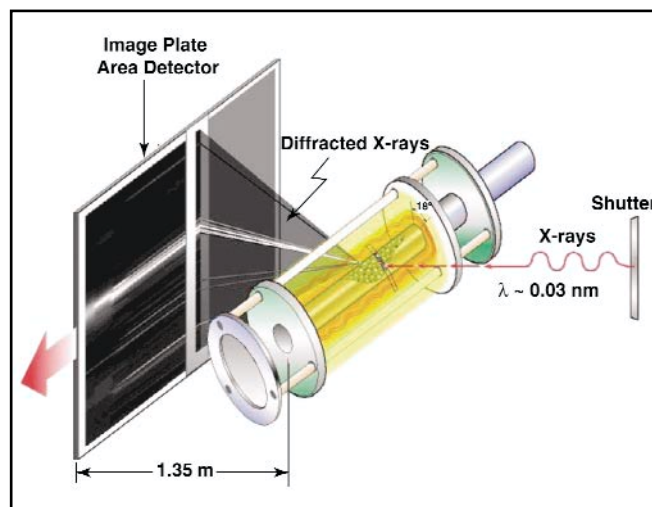


FIG. 1. A schematic representation of the high-temperature furnace and image plate geometry used in these experiments. The image plate is moved relative to the exit slot in the furnace. The exposure level is controlled by the translation rate of the plate and the time the beam shutter is left open, which varies from 2 to 10 s. The heating rate and dwell time at temperature can be controlled remotely and time and temperature recorded and correlated back to an exact position on the image plate. The heating rate can be varied continuously up to 50 K/min with a maximum furnace temperature of 1773 K.

x-rays was employed (Fig. 1). The detector was a  $200 \times 250$  mm Fuji image plate with pixel dimensions of  $100 \mu\text{m} \times 100 \mu\text{m}$ . The image plates were translated across a 1-mm vertical slit aligned with the long dimension of the plate. Each spectrum was obtained by translating the plate 3 mm with the x-ray shutter open. The translation rate was 2.0 mm/s for a total exposure time of 1.5 s. The sample was

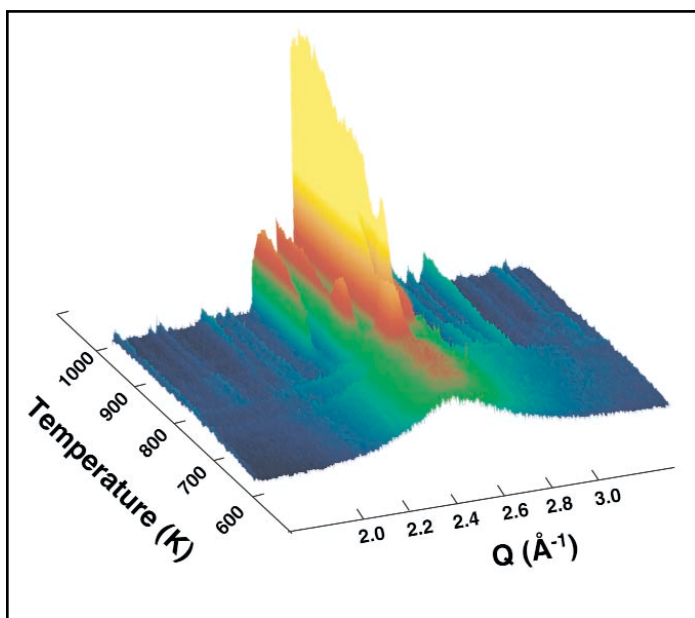


FIG. 2. 3-D surface plots showing the devitrification of  $\text{Ti}_{34}\text{Cu}_{47}\text{Zr}_{11}\text{Ni}_8$  when heated at 40 K/min.

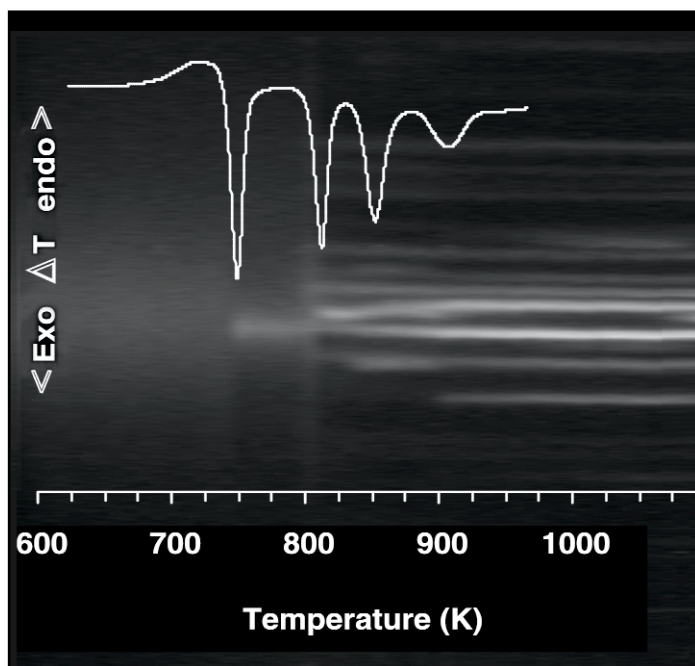


FIG. 3. Comparison of the image plate (increasing  $2\theta$  down) to the thermal analysis for identical heating rates of 40 K/min.

rotated  $\pm 18^\circ$  during the exposure to improve powder averaging. Individual spectra were then obtained by averaging the 30-pixel-wide columns. The actual diffraction data were collected approximately every 10 s while heating at 40 K/min between 623 and 1073 K. Intensity correction was determined using NBS intensity standard 674  $\text{Al}_2\text{O}_3$  taken in

identical fashion. In this manner, up to 47 spectra could be obtained on each image plate. IDL software was used to construct surface plots by interpolating the sequential  $2\theta$  versus intensity scans. Two similar metallic glass alloys were used:  $\text{Ti}_{34}\text{Cu}_{47}\text{Zr}_{11}\text{Ni}_8$  and  $\text{Ti}_{33}\text{Cu}_{47}\text{Zr}_{11}\text{Ni}_8\text{Si}_1$ . Samples of each composition were prepared as powders using high-pressure gas atomization. As discussed by Choi-Yin et al.[1], the addition of Si to Ti-Cu-Zr-Ni metallic glasses increases the onset of primary crystallization ( $T_x$ ) and extends the supercooled liquid region.

These three-dimensional surface plots provide a comprehensive impression of structural evolution during heating (Fig. 2). At lower temperatures (e.g., 773 K), the time-resolved data do not show the primary crystallization peak that developed during heating for 24 hr at the same temperature. At intermediate temperatures of 973 K, the continuous heating diffraction data are comparable to the data from the sample annealed for 24 hr, but further heating to 1073 K again shows that the continuously heated sample did not fully crystallize. Despite the likely higher diffusion rate at 1073 K, other factors (e.g., diffusion distances due to prior crystallization) must be retarding final crystallization during continuous heating.

Time-resolved x-ray diffraction detects the formation of nonequilibrium phases that may not be observable with traditional heat-and-quench techniques [2]. Here we demonstrated that the thermal events observed while  $\text{Ti}_{34-x}\text{Cu}_{47}\text{Zr}_{11}\text{Ni}_8\text{Si}_x$  metallic glasses at 40 K/min in the DSC do not necessarily correspond to equilibrium phases. Yet, a direct comparison of the DSC data and the image plate reveals a one-to-one correspondence of the thermal events to phase changes observed by x-ray diffraction. (Fig. 3).

The work at Ames Laboratory was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, through Iowa State University under Contract No. W-7405-ENG-82. The Midwest Universities Collaborative Access Team (Mu-CAT) sector at the APS is also supported by BES through Ames Laboratory under Contract No. W-7405-ENG-82. Use of the Advanced Photon Source was supported by BES under Contract No. W-31-109-ENG-38.

Principal publication: "Time-Resolved Studies of  $\text{Ti}_{3+x}\text{Cu}_{47}\text{Zr}_{11}\text{Ni}_8\text{Si}_x$  Metallic Glass Devitrification Using High Temperature X-ray Powder Diffraction," J. Non-Crystal. Solids (2001) in press.

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